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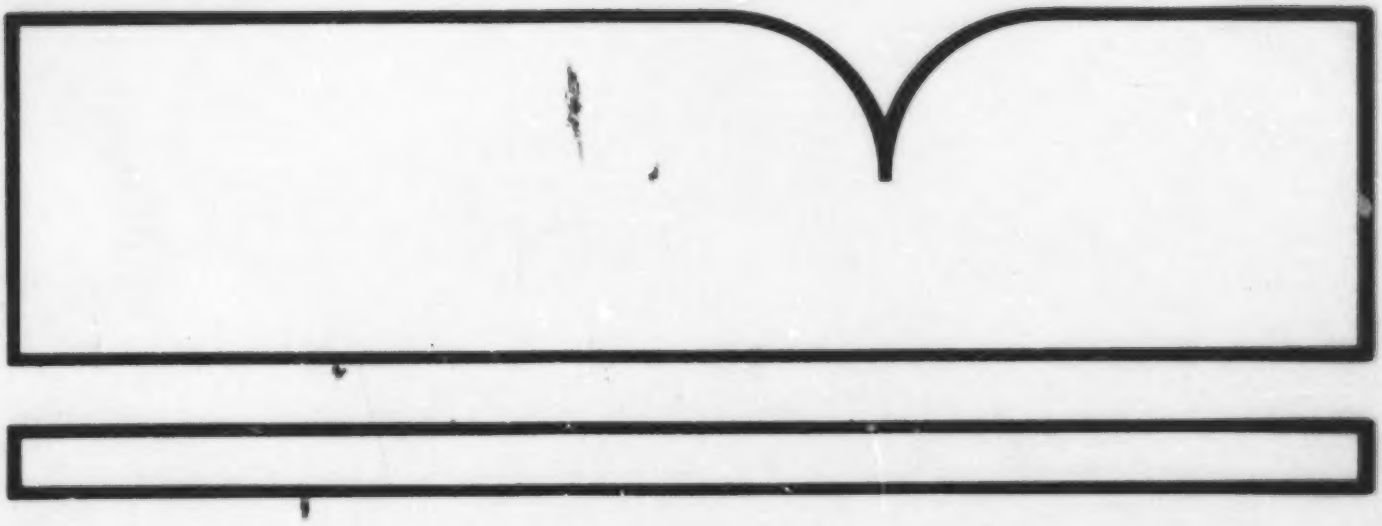

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16. ABSTRACT

Optimization of a HERL-designed 1-L closed-loop-stripping (CLS) system, using variations of sample water bath temperatures and purging times, was accomplished by spiking five 1-chloroalkanes (C_6, C_8, C_{12}, C_{16}, and C_{18}) into low organic Milli-Q reagent water to determine the recovery efficiency of each. Average recovery of the C_6, C_8, C_{12}, and C_{16} chloroalkanes exceeded 97% after CLS of water samples for 2 h at a sample bath temperature of 40 °C; the C_{18} chloroalkane's average recovery was 63% under the same conditions. Once operating conditions of purging time and water bath temperature were determined, on the basis of optimum recovery of the 1-chloroalkanes, recovery studies of a 22-compound standard mixture of organics were initiated by using two 1-L CLS devices of different design.

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Optimization of Purging Efficiency and Quantification of Organic Contaminants from Water Using a 1-L Closed-Loop-Stripping Apparatus and Computerized Capillary Column GC/MS

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■ Optimization of a HERL-designed 1-L closed-loop-stripping (CLS) system, using variations of sample water bath temperatures and purging times, was accomplished by spiking five 1-chloroalkanes (C_6, C_8, C_{12}, C_{16}, and C_{18}) into low organic Milli-Q reagent water to determine the recovery efficiency of each. Average recovery of the C_6, C_8, C_{12}, and C_{16} chloroalkanes exceeded 97% after CLS of water samples for 2 h at a sample bath temperature of 40 °C; the C_{18} chloroalkane's average recovery was 63% under the same conditions. Once operating conditions of purging time and water bath temperature were determined, on the basis of optimum recovery of the 1-chloroalkanes, recovery studies of a 22-compound standard mixture of organics were initiated by using two 1-L CLS devices of different design.

Introduction

CLS and computer-assisted capillary column GC/MS have been used routinely in this laboratory for the past 5 years to analyze organic compounds at the parts per trillion (nanograms per liter) level. Most of the compounds detected were in the 50–400 molecular weight range. Validation and applications of CLS as described by Grob (*1*) were discussed previously (*2–4*). In these previous studies (*2, 3*) a CLS device consisting of a 3.8-L (1 gallon) jug and computer-assisted glass capillary GC/MS and automatic quantitation procedures based on single mass ion quantification were used to provide results from repetitive CLS of standard compounds in water at the 10–100 ng/L level for statistical evaluation. Single ion quantification was used to resolve the effects of overlapping and coeluting GC peaks. Quantification is based on the ion current area of a single selected mass ion in a given mass spectrum, instead of the area produced by the summation of all ions in the mass spectrum. This ion is usually unique to a compound that may coelute with one or more compounds to produce ambiguous mass spectra. Statistical results (*3*) using the 1-gallon CLS device showed relatively low recovery efficiencies for many of the test compounds (average 45%) with an average relative standard deviation (RSD) of 30%. It was thought that the observed low recovery of higher molecular weight compounds and the imprecision of the 1-gallon CLS device could be improved by (1) purging a smaller volume with the same system, (2) better controlling the temperature of the gas entering the filter and of the filter itself, (3) increasing the temperature of the sample water bath, and (4) eliminating as much metal as possible in the closed loop between the sample bottle and the activated carbon trap. Figure 1 shows the 1-L CLS system currently in use in this laboratory. This paper discusses the optimization of the 1-L CLS system using variations of the four experimental parameters above as determined by optimum recovery of 1-chloroalkanes. Results from a commercial CLS system are also discussed and compared with the HERL 1-L CLS system. All accuracy and precision data in this report involve the use of the total analytical method, including all operations from the stripping of test compounds in water to the automatic computerized quantification of these compounds by the capillary GC/MS data system.

Experimental Section

Description of the 1-L CLS System. We have taken the CLS system discussed by Coleman (*2, 3*) and rebuilt and modified the apparatus so that it measures purgeable organics in 1-L samples instead of 1-gallon samples (see Figure 1). Air is continually recirculated through the closed-loop system by means of a pump (Metal Bellows Corp. Model MB-21). Air flows from the pump, through $^1/_8$-in. (3 mm) stainless steel tubing and a metal frit, and bubbles through the water sample which is immersed in a thermostatically controlled water bath (MGW–Lauda Model T1). To accomodate the inlet and exit lines, the poly(tetrafluorethylene) (PTFE) liner is removed from the sample bottle (1-L Wheaton/Kimler graduated culture media bottle) cap and a $^3/_4$-in. (20 mm) hole is drilled through it. The $^1/_8$-in. stainless steel inlet and exit lines are silver soldered to a stainless steel disk of the same inside diameter as the bottle cap. The disk with air lines attached is placed into the bottle cap; the bottom of the disk is covered with a PTFE washer; and the cap is screwed firmly onto the 1-L bottle. The sparging device, which includes the inlet and exit lines, bottle cap, frit, disk, and washer, is very similar to the one reported by Coleman (*2*). The $^1/_8$-in. stainless steel tube exiting the bottle is just long enough to allow it to be connected to the bottom of a Graham condenser (Corning) modified by attaching a $^1/_4$-in. glass tube. A $^1/_4$–$^1/_8$-in. stainless steel Swagelok reducing union with PTFE ferrules is used to make this connection. The condenser is heated with 95 °C water from a recirculating bath (Haake Model FJ). The top portion of the condenser is also modified by removing 2.5 in. of glass tubing beyond the water jacket, replacing it with

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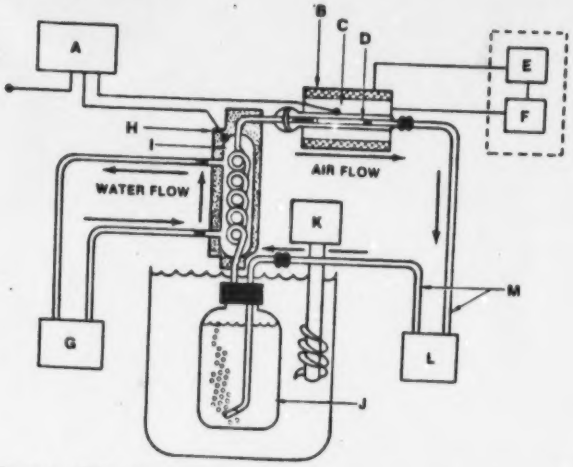

Figure 1. HERL closed-loop-stripping apparatus (Aug 1980). Key: (A) temperature monitor; (B) heater block insulation; (C) aluminum heating block with cartridge heater; (D) glass filter holder with carbon filter; (E and F) temperature controller (maintains 50 °C); (G) thermostatically controlled water circulator for I (set at 95 °C); (H) foam insulation; (I) glass condensing column; (J) 1-L sample bottle; (K) thermostatically controlled water bath circulator (set at 40 °C); (L) Metal Bellows air pump; (M) $^1/_8$-in. stainless steel tubing.

the male half of the glass filter holder, and making a 90° bend. The activated carbon filter is placed in the female half of the filter holder, and the two halves of the holder are joined with spring clips. The filter and filter holder rest in an aluminum block $3 \times 3^1/_2 \times 1^3/_4$ in. (7.6 × 9 × 4.5 cm) heated and monitored by an Omega Model 4001 JC temperature controller. The $^1/_4$-in. (6 mm) glass exit end of the filter holder is connected to the stainless steel tubing leading to the pump with a Swagelok reducing union as previously described.

Optimization of the 1-L CLS system was accomplished by performing replicate CLS GC/MS analyses of five 1-chloroalkanes (C_6, C_8, C_{12}, C_{16}, and C_{18}) at sample water bath temperatures of 30–50 °C in increments of 5 °C. The condenser recirculating water temperature was maintained at 95 °C. The temperature of the carbon filter was maintained at 10 °C above the selected temperature of the sample bath water. The reference amount of each of the first four 1-chloroalkane standards, from which recovery efficiencies were determined, was 52 ng. The amount of C_{18} was 104 ng. The quantitation reference internal standard was 1-chlorododecane. Quantification was based on selected single ion areas relative to the selected single ion area of 1-chlorododecane (*2, 3*). The percent recovery of each standard was then determined by comparing the computer quantitated amount from the purged water samples to the amount in the spiked water, according to the following formula:

$$\% \text{ recovery} = \frac{\text{amount calculated (ng)}}{\text{amount spiked (ng)}} \times 100 \quad (1)$$

Recovery Studies. Once optimum purging conditions were determined as described in the above study, recovery studies were conducted by using a mixture of 22 reference compounds spiked in water. Since all organic compounds have varying vapor pressures and solubilities in water and since all compounds are not 100% purged from the water by CLS, experimental response factors, which include GC/MS response and CLS recovery factors, must be determined in order to measure levels of organic ompounds in environmental samples.

Seven repetitive GC/MS analyses of the direct injections of a 22-compound standard mixture of organics were performed to establish sets of average relative retention times (RRTs) and GC/MS reponse factors (RFs) for each compound. These values were entered into a computerized quantitation library. The use of the quantitation library to measure organics in water has been previously described (*2, 3*). Six repetitive CLS GC/MS analyses of water spiked with a 22-compound standard mixture were performed by using both CLS systems. RRT and RF values established in the above direct injection measurements were used to quantify and determine the recovery efficiency of each of the 22 compounds from water. The recovery of each compound was determined by using eq 1 above.

Reagents and Equipment. All solvents and chemicals used for the preparation of standard solutions were reagent grade.

Preparation of Standard Solutions. Stock solutions of the 22 test compounds and of the 1-chloroalkane standards were prepared in acetone. Aliquots of the acetone stock solutions were diluted with carbon disulfide to prepare the direct injection standards for GC/MS RRT and RF determinations. Standards and internal standards for spiking reagent water were diluted with acetone. An aliquot containing the five 1-chloroalkanes was added to each direct injection standard solution and to each water sample before CLS. The reference amounts for the 1-chloroalkanes including the quantitation reference standard, 1-chlorododecane, were the same as in the optimization study, above; the reference amounts of the direct injection standards and CLS standards were in the 20–30-ng range. Detailed preparation of standard solutions has been previously reported by Coleman (*3*).

Closed-Loop-Stripping Analysis. CLS analyses were performed at optimized temperatures on 1-L samples of water. Temperatures of 40, 50, and 95 °C were maintained for the sample bath water, carbon filter, and the recirculating condenser water, respectively, and for all analyses in the recovery studies. CLS was initiated by filling a sample container to capacity with Milli-Q water, decanting a small amount of the water down to the 1-L mark, adding 2 μL each of the acetone standard solution and the internal standard solution, and then assembling the purging apparatus. After placing the assembled purging apparatus and activated carbon trap in the closed loop, the pump was started and the sample was stripped of organics by recirculating the head space gas through the water sample and the carbon filter for 2 h. Sampling, stripping, and carbon filter extraction procedures, as used in this laboratory, are similar to the procedures described by Grob (*1*) and Coleman (*2*). Two microliters of the approximate 8 μL of collected carbon disulfide extract was used for GC/MS analysis. The amounts determined in this 2-μL sample were compared to the reference amounts of individual standards to calculate their recovery.

Computerized Fused Silica Capillary GC/MS System. GC/MS analyses and quantification results were performed on a Finnigan Model 3300 quadrupole mass spectrometer equipped with an Incos Model 2300 data system computer. A Carlo-Erba Fractovap 4160 gas chromatograph was equipped with a Grob-designed splitless injector and a 60 m long × 0.25 mm i.d. wall-coated-open-tubular fused silica SE-30 column. One end of the column was inserted into the MS ion source chamber just to the edge of the ion beam, by way of a transfer oven, the temperature of which was held at 270 °C.

Two microliters of each CLS extract was injected with the column vent of the splitless injector closed. The

column vent (20:1 ratio) was opened 30 s after injection. Grob's (5) hot needle injection technique was used for all analyses. The helium carrier gas flow rate was about 3 mL/min at 25 °C; the linear velocity through the GC column was 25 cm/s with a helium head pressure of 1.2 kg/cm^2 (17 psi) without a flow controller. The injector temperature was maintained at 260 °C. Samples were injected at 20 °C by cooling the GC oven with liquid nitrogen. After a 6-min hold at 20 °C, the oven temperature was programmed to 250 °C at a rate of 2 °C/min. Mass spectra were acquired from 14 to 450 amu at the rate of one scan per 2 s. The 20 °C initial column temperature and the 2 °C/min temperature program rate sufficiently retarded the elution of very volatile compounds to allow a 2-s scan rate. A total of 95% of all GC peaks had minimum elution times of 12 s, thus guaranteeing good ion distribution and representative mass spectra for identification and quantification. Experience in this laboratory has shown that the statistical variations for peak areas at faster scan times (i.e., 1 s) are not that different from a 2-s scan time when at least six samples of the GC peak are acquired by the data system. Peak area measurements and variations have been discussed previously (2, 3). The electron energy was 70 eV, and the source temperature was 90 °C. Source pressure was approximately 5×10^{-6} torr when the GC column temperature was 25 °C. Data acquisition was terminated after 3900 mass spectra (130 min) were obtained.

Quantification. Automatic computerized quantification procedures (3) based on selected single ions of a mass spectrum and the internal standard (IS) method of quantification were used to calculate the level of organics in direct injection standards and in CLS extracts. A computer quantitation library containing reference mass spectra of the 22 standard compounds and of 1-chlorododecane as the quantitation reference standard was established. In addition, the library contained RRT values, single ion RFs (relative to 1-chlorododecane), and reference amounts for each compound. The reference amount of 1-chlorododecane was 52 ng; its quantitation mass was m/z 91. Quantitation formulas used by the computer are shown in eq 2–4

$$\text{amount Z} = \frac{\text{single ion area Z} \times \text{IS amount}}{\text{single ion area IS} \times \text{RF(L)}} \quad (2)$$

(L) = library RF for Z

$$\text{amount Z in water} = \frac{\text{single ion area Z} \times \text{IS amount}}{\text{single ion area IS} \times [\text{RF(L)} \times \text{RE}]} \quad (3)$$

where RE is the recovery efficiency of Z and RE = % recovered/100 or

$$\text{amount Z in water} = \frac{\text{single ion area Z} \times \text{IS amount}}{\text{single ion area IS} \times \text{RF(L)}} \times \text{U1} \quad (4)$$

where U1 is a user parameter stored in the quantitation library as an amount multiplier equal to 1/RE. U1 may vary depending on the sample matrix. Therefore, recovery efficiencies must be determined for each sample matrix. Equation 4 is preferred when quantifying compounds in water samples, since U1 can be removed from the computer quantitation statement when direct injection standards are analyzed.

Previous studies (2, 3) have shown that the accuracy and precision of single ion quantification depend mainly on the stability of the MS when the data system is set to acquire a minimum of six samplings of a GC peak. The fact that the RFs are based on a single ion from the internal standard (m/z 91 of 1-chlorododecane) relative to a single ion in the mass spectrum of the compounds to be measured (ranging from m/z 91 to 284 in this study) mandates that the relative intensities of mass ions in a given spectrum should remain consistent in order to obtain reproducible RFs. There was generally a lower degree of accuracy and precision for those compounds quantified on mass ions above m/z 180. Such was the case for the polychlorinated benzenes and biphenyls, whose spectra have ions predominately from m/z 150 to 365.

Table I. Mean Percent Recovery[a] of 1-Chloroalkanes after CLS of 1 L of Water

	sample water bath temp, °C[b]	closed-loop-stripping time, h			
		0.5	1.0	1.5	2.0
1-chlorohexane	30	72	78	83	87
	35	77	72	81	86
	40	97	97	97	98
1-chlorooctane	30	62	74	81	86
	35	81	72	77	88
	40	97	97	98	98
1-chlorododecane[c]	30	53	67	80	83
	35	82	74	90	99
	40	98	98	99	99
1-chlorohexadecane	30	7	11	30	40
	35	27	46	73	98
	40	28	63	84	98
1-chlorooctadecane	30	2	2	6	10
	35	6	9	18	29
	40	8	15	27	63

[a] Based on triplicate analysis. [b] In each case, the filter holder temperature was adjusted to be 10 °C above the water bath temperature; the condenser water temperature was maintained at 95 °C. [c] Quantitation reference standard. At 40 °C and 2-h stripping time, the RSD was ±6% on the basis of six determinations.

Blanks. Procedural blanks were incorporated into the analytical scheme. Before analysis of actual samples, carbon filter blanks and CLS blanks of Milli-Q reagent water containing the five 1-chloroalkane standards were determined. All reported quantities were corrected for contaminants in the blanks.

Results and Discussion

Results of the 1-L optimization study based on the recovery of 1-chloroalkanes are shown in Table I. The data indicate that >95% of C_6, C_8 and C_{12} were recovered in the first 0.5 h of stripping and that >95% of C_{16} was recovered in 2 h of gas stripping of water samples at 40 °C. The recovery of C_{18} averaged 63% at 40 °C. Attempts were made to improve the recovery of C_{18} by increasing the sample water bath temperature to 45 and 50 °C (carbon filter at 55 and 60 °C, respectively). In both cases, the increase in stripping temperatures caused water vapor to condense in the trap. In viewing all parameters, a 40 °C bath temperature and a 2-h stripping time were considered to be optimum in order to recover these 1-chloroalkane standards with the greatest efficiency. We recognize that the CLS system could not be optimized for all compounds under a single set of conditions when doing broad spectrum analyses. However, the group of 1-chloroalkanes (C_6–C_{18}) represented a range of molecular weights from 120 to 288 and boiling points from 134 to 348 °C. It is conceivable that longer stripping times at 40 °C would improve the recovery of the C_{18} chloroalkane and of higher molecular weight compounds, but increased analysis time would also

Table II. Precision of Repetitive Direct Injection Study

compound	quantitation mass m/z	amt injected, ng	mean[a] GC/MS response factor	RSD, %
thiophene	84	25.4	2.416	5.9
dibromochloromethane	129	29.4	0.847	4.7
styrene	104	21.8	2.884	5.5
isopropylbenzene	105	24.2	3.923	4.9
2-chlorotoluene	91	25.9	2.932	4.2
bis(2-chloroethyl) ether	93	24.4	1.871	3.7
α-methylstyrene	118	21.6	2.003	6.0
1,4-dichlorobenzene	146	19.8	1.950	7.1
2-ethyl-1,3-dimethylbenzene	119	24.1	4.410	4.6
4-chloro-*o*-xylene	105	25.7	2.516	4.6
1,1-dimethylindan	131	21.7	3.512	4.6
p-methylphenol	107	26.6	2.323	3.4
tetrahydronaphthalene	104	23.4	2.428	4.7
1,2,4-trichlorobenzene	180	23.2	1.178	7.3
hexachloro-1,3-butadiene	225	26.9	0.347	10.1
2-methylbiphenyl	168	24.4	1.635	7.0
1,6-dimethylnaphthalene	156	24.2	1.953	5.8
2-isopropylnaphthalene	155	22.7	3.562	5.7
pentachlorobenzene	250	26.1	0.400	12.0
hexachlorobenzene	284	20.1	0.265	11.3
2,2′,4,4′,6,6′-hexachlorobiphenyl	145	27.0	0.202	6.0
2,2′,4,5,5′-pentachlorobiphenyl	254	28.2	0.141	11.3
1-chlorododecane[b]	91	52.2	1.000	

[a] Based on seven determinations. [b] Quantitation reference standard.

Table III. Recovery and Precision Data for Repetitive Purge Study—HERL 1-L CLS System

compound	std amt, ng	mean[a] recovered amt, ng	range	recovery efficiency, %	RSD, %
thiophene	25.4	8.8	7.2-10.9	34.6	15.9
dibromochloromethane	29.4	16.6	13.3-21.0	56.5	12.6
styrene	21.8	17.4	15.9-19.6	79.8	6.9
isopropylbenzene	24.2	25.9	23.8-28.7	107.0	7.7
2-chlorotoluene	25.9	23.3	21.6-26.9	90.0	7.7
bis(2-chloroethyl) ether	24.4	2.8	2.6-3.5	11.6	10.7
α-methylstyrene	21.6	19.4	18.1-21.6	89.9	6.2
1,4-dichlorobenzene	19.8	18.3	16.4-20.6	92.5	8.2
2-ethyl-1,3-dimethylbenzene	24.1	22.3	20.8-24.7	92.4	5.8
4-chloro-*o*-xylene	25.7	21.8	20.2-26.0	84.8	9.2
1,1-dimethylindan	21.7	23.8	21.6-26.2	109.5	7.1
p-methylphenol	26.6	ND[b]			
tetrahydronaphthalene	23.4	23.1	20.2-26.3	98.6	10.4
1,2,4-trichlorobenzene	23.2	19.2	17.6-20.9	82.9	7.3
hexachloro-1,3-butadiene	26.9	30.9	27.4-34.3	113.8	9.2
2-methylbiphenyl	24.4	24.8	22.0-27.1	101.4	7.7
1,6-dimethylnaphthalene	24.2	9.5	7.6-11.2	39.3	11.6
2-isopropylnaphthalene	22.7	20.6	18.8-22.3	90.8	6.3
pentachlorobenzene	26.1	12.4	10.7-14.3	47.7	11.3
hexachlorobenzene	20.1	6.2	5.0-7.4	31.1	12.9
2,2′,4,4′,6,6′-hexachlorobiphenyl	27.1	28.2	26.1-32.3	104.3	7.1
2,2′,4,5,5′-pentachlorobiphenyl	28.2	23.0	17.8-27.6	81.5	14.3

[a] Based on six purging analyses using single ion quantification. [b] ND = not detected.

be impractical in most laboratories where several samples are analyzed daily.

The standard deviations around the norm were calculated for the RFs, amounts, and recovery efficiencies by using data from both CLS systems. Table II shows the precision of the repetitive direct injection study. The individual RFs obtained by single ion quantification of the listed masses in Table II had RSDs ranging from 3.4% to 12.0%. Compounds quantified on m/z ions 84–168 had RSDs of 3.4–7.1%; those quantified on m/z ions 180–284 had RSDs of 7.3–12.0%. The average RSD for RFs of all compounds in the direct injection study was 6.4%. Previous studies (*2*, *3*), where standard deviations were calculated for GC/MS peak areas of these standards, showed that single ion areas had RSDs of 13%. However, and most importantly, the internal standard method of quantitation compensated for these variations when the amounts were calculated by the computer.

Recovery and precision data from the 1-L CLS systems are shown in Tables III and IV. Table V summarizes the data in Tables III and IV and compares it to the recovery data from the 1-gallon CLS system (*3*). In general, Table V shows that the two 1-L CLS systems were about equal in performance, with the HERL system having a slight edge in overall method precision. Mean recovery efficiencies (percent) and RSDs, for 20 compounds that were common to each study, were 48% (28% RSD), 80% (9% RSD), and 83% (13% RSD), respectively, for the 1-gallon, 1-L HERL, and 1-L commercial CLS systems.

This laboratory recently participated in two collaborative studies using closed-loop stripping. One study involved the analysis of purgeable aromatics at the 7–65 ng/L level, and the other was for the analysis of organic compounds causing taste and odor at the 3–35 ng/L level.

Table IV. Recovery and Precision Data for Repetitive Purge Study—Commercial 1-L CLS System

compound	std amt, ng	mean[a] recovered amt, ng	range	recovery efficiency, %	RSD, %
thiophene	25.4	13.5	10.0-15.8	53.7	14.1
dibromochloromethane	29.4	23.3	18.1-26.9	79.3	12.4
styrene	21.8	17.9	13.8-22.7	82.1	15.1
isopropylbenzene	24.2	25.2	20.9-30.9	104.3	13.5
2-chlorotoluene	25.9	23.2	18.9-27.8	89.4	12.1
bis(2-chloroethyl) ether	24.4	4.4	3.5-4.8	18.0	9.1
α-methylstyrene	21.6	18.3	14.8-22.6	84.8	13.7
1,4-dichlorobenzene	19.8	18.2	14.8-20.7	91.7	11.5
2-ethyl-1,3-dimethylbenzene	24.1	22.2	18.4-25.6	92.0	10.8
4-chloro-*o*-xylene	25.7	21.1	17.4-25.6	85.9	12.2
1,1-dimethylindan	21.7	23.1	19.3-27.1	106.0	11.7
p-methylphenol	26.6	ND[b]			
tetrahydronaphthalene	23.4	22.9	17.8-27.1	97.7	12.2
1,2,4-trichlorobenzene	23.2	19.9	16.3-23.9	85.9	11.0
hexachloro-1,3-butadiene	26.9	29.7	24.4-35.2	110.5	12.1
2-methylbiphenyl	24.4	25.4	22.8-27.8	104.2	7.5
1,6-dimethylnaphthalene	24.2	12.2	9.6-15.7	50.4	18.9
2-isopropylnaphthalene	22.7	21.7	19.8-24.7	95.8	7.8
pentachlorobenzene	26.1	13.4	9.9-20.2	51.5	25.4
hexachlorobenzene	20.1	7.3	4.9-12.1	36.5	32.9
2,2',4,4'6,6'-hexachlorobiphenyl	27.0	31.6	28.5-37.3	117.0	8.9
2,2',4,5,5'-pentachlorobiphenyl	28.2	24.8	17.9-30.2	88.0	21.0

[a] Based on six purging analyses using single ion quantification. [b] ND = not detected.

Table V. Recovery Efficiency Comparisons of CLS Devices

	1 gallon		HERL 1 L		commercial 1 L	
compound	recovery efficiency,[a] %	RSD, %	recovery efficiency,[b] %	RSD, %	recovery efficiency,[b] %	RSD, %
thiophene	NA[c]		34.6	15.9	53.3	14.1
dibromochloromethane	15.7	71.3	56.5	12.6	79.3	12.4
styrene	53.7	22.0	79.8	6.9	82.1	15.1
isopropylbenzene	72.2	26.9	107.0	7.7	104.3	13.5
2-chlorotoluene	54.3	22.3	90.0	7.7	89.4	12.1
bis(2-chloroethyl) ether	0.4	75.0	11.6	10.7	18.0	9.1
α-methylstyrene	56.4	22.7	89.8	6.2	84.8	13.7
1,4-dichlorobenzene	71.2	26.5	92.5	8.2	91.7	11.5
2-ethyl-1,3-dimethylbenzene	NA		92.4	5.8	92.0	10.8
4-chloro-*o*-xylene	52.5	23.4	84.8	9.2	85.9	12.2
1,1-dimethylindan	73.4	25.6	109.5	7.1	106.0	11.7
p-methylphenol	ND[d]		ND		ND	
tetrahydronaphthalene	53.6	23.1	98.6	10.4	97.7	12.2
1,2,4-trichlorobenzene	55.1	25.4	82.9	7.3	85.9	11.0
hexachloro-1,3-butadiene	89.4	28.7	113.8	9.2	110.5	12.1
2-methylbiphenyl	51.9	28.3	101.4	7.7	104.2	7.5
1,6-dimethylnaphthalene	12.3	36.6	39.3	11.6	50.4	18.9
2-isopropylnaphthalene	49.1	26.7	90.8	6.3	95.8	7.8
pentachlorobenzene	26.0	37.7	47.7	11.3	51.5	25.4
hexachlorobenzene	11.9	65.5	31.1	12.9	36.5	32.9
2,2',4,4',6,6'-hexachlorobiphenyl	58.7	30.5	104.3	7.1	117.0	8.9
2,2',4,5,5'-pentachlorobiphenyl	18.8	39.9	81.5	14.3	88.0	21.0

[a] Average of 16 determinations. [b] Average of six determinations. [c] NA = not analyzed. 2-Methylthiophene and 2-ethyl-1,4-dimethylbenzene were in the 1-gallon study. [d] ND = not detected.

The reported results from both studies were all acceptable and within 95% confidence limits. It is obvious from these studies that truly low concentrations of organic compounds can be accurately measured by CLS.

Summary and Conclusions

A redesigned and modified 1-L CLS system was optimized for maximum purging efficiency of 1-chloroalkane standards spiked in water. The optimum conditions established to recover all 1-chloroalkanes with the greatest efficiency were 40 °C for the sample bath water, 50 °C for the activated carbon trap, 95 °C for the Graham condenser, and 2 h for the stripping time. Under these sets of conditions, >95% of 1-chlorohexane, 1-chlorooctane, 1-chlorododecane, 1-chlorohexadecane, and 63% of 1-chlorooctadecane were recovered from replicate CLS analyses.

The above optimized conditions were used for CLS of 1-L water samples spiked with a 22-compound standard mixture in order to determine recovery efficiency factors from two different 1-L CLS systems. The CLS carbon extracts were analyzed by fused silica capillary column GC/MS. Quantification procedures, using single ion quantification and the internal standard method of analysis, were used to determine recovery results.

Quantification and recovery results from the two 1-L and the previously reported 1-gallon CLS systems were compared. The two 1-L CLS systems were about equal in overall method recovery efficiency for the test compounds. The average recovery efficiency for all compounds using

the 1-gallon CLS system was about half that of the 1-L systems. Comparing the results from the 1-gallon CLS study to the optimized 1-L CLS study, the mean recovery efficiency (percent) and RSD were 48% (28% RSD) and 80% (9% RSD), respectively. Of the 22 compounds tested with the optimized 1-L CLS system, 10 had recoveries >90% including a hexachlorobiphenyl isomer (M_r 358).

This report supports previous CLS applications papers (2–4) demonstrating that CLS–capillary column GC/MS is an excellent method to measure many toxic organics in drinking water and in groundwater. For quantitative results, recovery efficiencies of individual compounds must be determined in the same matrix as the sample matrix.

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Registry No. C, 7440-44-0; water, 7732-18-5; 1-chlorohexane, 544-10-5; 1-chlorooctane, 111-85-3; 1-chlorododecane, 112-52-7; 1-chlorohexadecane, 4860-03-1; 1-chlorooctadecane, 3386-33-2; thiophene, 110-02-1; dibromochloromethane, 124-48-1; styrene, 100-42-5; isopropylbenzene, 98-82-8; 2-chlorotoluene, 95-49-8; bis(2-chloroethyl) ether, 111-44-4; α-methylstyrene, 98-83-9; 1,4-dichlorobenzene, 106-46-7; 2-ethyl-1,3-dimethylbenzene, 2870-04-4; 4-chloro-*o*-xylene, 615-60-1; 1,1-dimethylindan, 4912-92-9; *p*-methylphenol, 106-44-5; tetrahydronaphthalene, 119-64-2; 1,2,4-trichlorobenzene, 120-82-1; hexachloro-1,3-butadiene, 87-68-3; 2-methylbiphenyl, 643-58-3; 1,6-dimethylnaphthalene, 575-43-9; 2-isopropylnaphthalene, 2027-17-0; pentachlorobenzene, 608-93-5; hexachlorobenzene, 118-74-1; 2,2′4,4′,6,6′-hexachlorobiphenyl, 33979-03-2; 2,2′,4,5,5′-pentachlorobiphenyl, 37680-73-2.

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Statistical Approach for Deciding If Mussels (*Mytilus edulis*) Have Been Collected from a Water Body Polluted with Trace Metals

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■ A statistical approach is developed to decide whether specimens of *Mytilus edulis* (mussels), a sentinel organism for heavy metals, are inhabiting a water body that can be classified as polluted. Principal component analysis was applied to the correlation matrix of variates (Mn, Fe, Cu, Zn, and Pb concentrations, dry weight, wet weight, shell length, day/season of collection) measured in specimens collected monthly over a 12-month period from an unpolluted location in an estuary of southwestern British Columbia. Using the principal component scores determined for this set as a reference, a procedure is developed to decide whether similarly measured variates and related principal component scores for mussels collected from other locations indicate if these other water bodies were "polluted" with heavy metals.

Introduction

Mytilus edulis (mussels) are well recognized as a valuable monitor of trace-metal pollution of estuarine waters (*1–3*). However, a necessary part of monitoring environments is deciding whether or not they are polluted on the basis of trace-metal body burdens in the mussels. Goldberg et al. (*1*) have suggested that concentrations 10 times those found in base-line studies of mussels collected from nonpollutant waters may be a suitable criterion to denote a polluted water body, but this hypothesis should be tested. In a previous study (*4*), we have suggested that a statistical approach could be used to resolve such issues by using what is known as a generalized distance function (*5*). For a study in which the concentration of only one element is of interest in deciding if a water body is polluted or not, the square of the standard score, z^2, can be used:

$$z^2 = (x - m)^2/s^2 \qquad (1)$$

where x is the measured value of the concentration of the element of interest in the specimen selected from a habitat of unknown quality and m and s^2 are, respectively, the mean and variance of the concentration of the element in specimens from a reference habitat having an acceptably low trace-metal concentration. The χ-square distance function is equal to z^2, and the probability, P, for a given χ-square can be calculated in order to estimate the proportion of organisms of the reference sample that reside as close to or closer to the mean than organisms collected from the habitats of unknown quality (*5*). Obviously, large positive differences between x and m results in large z scores. These, in turn, yield large χ-square distances, resulting in low probabilities that the sample in question is representative of the reference population used to derive m and s^2 (*5*).

Unfortunately, many physiological functions in bivalves are related to their size, their state of the gametogenic cycle, or both. Bayne et al. (*6*) have recently discussed this phenomenon with respect to selecting the required number of animals in order to use an analysis of covariance for detecting differences among populations with respect to oxygen consumption in the bivalve *Scrobicularia plana*. Metal concentrations in mussels are also well correlated

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